

The University of Chicago

HALOGENATION OF ALKYL HALIDES

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1936

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MARTELL MAURICE GLADSTONE

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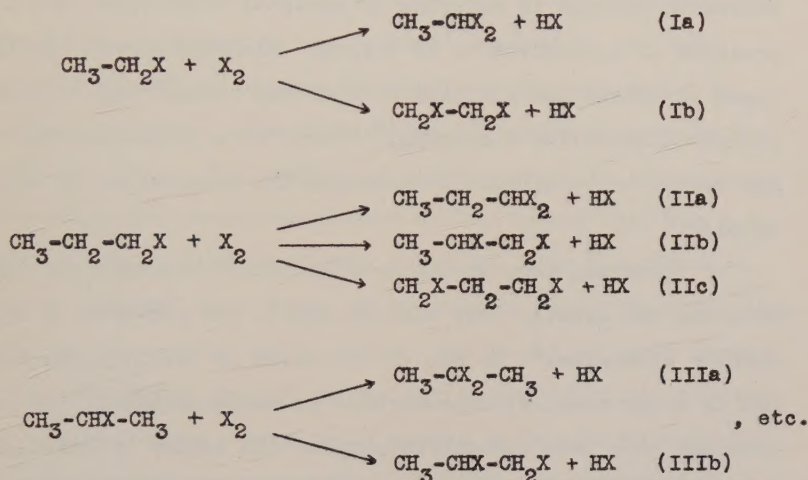
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HALOGENATION OF ALKYL HALIDES

The treatment of an alkyl halide (RX) with one mole of a halogen (X_2) may conceivably lead to the formation of any or all of the possible isomeric dihalides, according to the following equations:



The position taken by the second halogen atom in such reactions may be determined by statistical probability, in which case mixtures should be obtained, or by directive forces within the molecules, in which case pure products might be obtained. The chlorination of ethyl chloride and the bromination of ethyl bromide under carefully controlled conditions yields either the pure 1,1- or the pure 1,2-dihalide (Ia and Ib, respectively). The 1,2-dihalide is obtained in the presence of certain metallic catalysts and the other isomer is formed in the absence of such

catalysts.¹ Therefore it is apparent that the position taken by the entering atom depends upon the catalyst and directing forces within the molecule, and not upon chance. We shall define the "normal" product as the one obtained in the absence of catalysts and the "abnormal" product as the isomeric product formed in the presence of certain catalysts.

In order to interpret such reactions and to extend the findings to other halides, it is necessary to know how the substitution process is affected by external conditions such as the presence of a catalyst or of oxygen. Although oxygen has been found to affect the addition of hydrogen bromide and bromine to certain unsaturated compounds,² recent work indicates that oxygen has little or no effect in directing the bromination of ethyl bromide.³

Previous work on the bromination of n-propyl and isopropyl bromides has usually been carried out in the presence of salts of iron or aluminium.⁴ In one or two cases no catalyst was added, but in every case, with or without an added catalyst, the products obtained have been 1,2-dibromopropane and higher bromination

¹ Hofmann, Jahresbericht, 1860, 346; Caventou, Ann., 120, 322 (1861); Tawildarow, Ann., 176, 12 (1875); Denzel, Ann., 195, 189 (1879); V. Meyer and Müller, Ber., 24, 4247 (1891); J. prakt. Chem., (2) 46, 161 (1892); V. Meyer and Petrenko-Kritschenko, Ber., 25, 3304 (1892); Mouneyrat, Bull. soc. chim., (3) 19, 497 (1898); Regnault, Ann., 33, 312 (1840); Staedel, J. prakt. Chem., (2) 80, 303 (1909); D'Ans and Kautzsch, J. prakt. Chem., (2) 80, 310 (1909).

² Kharasch and others, J. Am. Chem. Soc., 55, 2468, 2521, 2531 (1933); 56, 712, 1212, 1243, 1642, 244 (1934); 57, 2463 (1935); Chem. and Ind., 1935, 989; Ashton and Smith, J. Chem. Soc., 1934, 435, 1308; Shultze, J. Am. Chem. Soc., 56, 1552 (1934).

³ Kharasch, Tanner and Hinckley, unpublished work.

⁴ Linnemann, Ann., 136, 51 (1865); 161, 41 (1872); V. Meyer and Müller, op. cit.; V. Meyer and Petrenko-Kritschenko, op. cit.; Mouneyrat, Bull. soc. chim., (3) 19, 803 (1898); Bodroux, Bull. soc. chim., (3) 25, 241 (1901).

products. No 1,1-,1,3-, or 2,2-dibromopropane has ever been reported as a product of these reactions. Similarly, chlorination of n-propyl chloride in the presence of catalysts yields 1,2-dichloropropane.⁵ No 1,1- or 1,3-dichloropropane propane has been reported. However, by the chlorination of isopropyl chloride in sunlight, two dichlorides, namely, 1,2- and 2,2-dichloropropane, are obtained as a mixture containing from 20% to 66% of the former.⁶

The halogenation of the propyl halides was undertaken for the purpose of establishing the "normal" conditions for the reaction and to determine what the reaction products would be under such conditions. The bromination of isopropyl bromide was investigated first. The product of this reaction in the absence of metal salts is 2,2-dibromopropane (IIIa) rather than the 1,2-dibromo compound (IIIb) previously reported. The 2,2-dibromopropane is obtained when oxygen is present or absent and also when the reaction is carried out in either the liquid or vapor phase. Therefore, the first product of the normal substitution reaction is 2,2-dibromopropane. If a small amount of ferric chloride is added to the reaction mixture, the substance obtained is 1,2-dibromopropane.

These results are in accord with Markownikoff's well-known rule and with one of Mereshkowsky's rules, which state, respectively, that on halogenating an alkyl halide the entering halogen atom becomes attached to the carbon atom to which a halogen atom

⁵Mouneyrat, Ann. de chim., (7) 20, 522 (1900); Bull. soc. chim., (3) 21, 618 (1899).

⁶Friedel and DeSilva, Compt. rend., 73, 1379 (1871); Bull. soc. chim., (2) 16, 3 (1871).

is already attached,⁷ and that the direction of substitution is affected by the presence of a catalyst.⁸ Markownikoff and Städel and Denzel⁹ arrived at their conclusions from experiments on the halogenation of ethyl bromide and ethyl chloride. V. Meyer and Petrenko-Kritschenko, working with the propyl and butyl compounds in the presence of catalysts, found that the entering halogen atom became attached to the carbon atom next to that holding the first halogen atom,¹⁰ whereupon Markownikoff promptly, and properly, objected to the "abnormal" conditions which had prevailed.¹¹

These rules are empirical and predict, but do not explain, the products of normal substitution. The same results are predicted and in some measure explained by a proper consideration of the relative electronegativities of the different groups in the substances under discussion.¹² The substitution of a more electronegative radical for a hydrogen atom of a methyl group decreases the electronegativity of the methyl carbon atom; i.e., that carbon atom holds its electrons less firmly and is therefore more easily oxidized than the original methyl carbon atom.

⁷This rule is quoted from Markownikoff, "Materiellen zu der Frage über die gegenseitigen Einflüsse der Atome in chemische Verbindungen," (Kazan, 1859), by Mereshkowsky, Ann., 431, 113 (1923).

Städel and Denzel, unaware of Markownikoff's work, independently arrived at the same conclusion. Ann., 195, 180 (1879).

⁸Mereshkowsky, Ann., 431, 113 (1923).

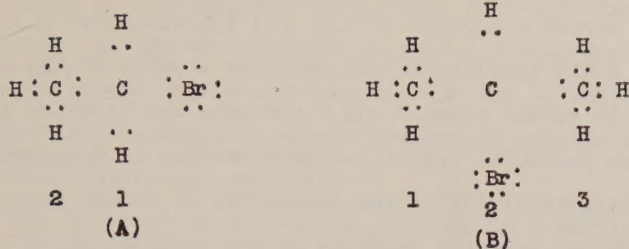
⁹Loc. cit.

¹⁰V. Meyer and Petrenko-Kritschenko, loc. cit.

¹¹Markownikoff, J. Russ. Phys.-Chem. Soc., 25, (2) 35 (1893); cf. Mereshkowsky, loc. cit.

¹²This notion is discussed by Kharasch and Rheinmuth, J. Chem. Ed., 5, 404 (1928); 8, 1725 (1931).

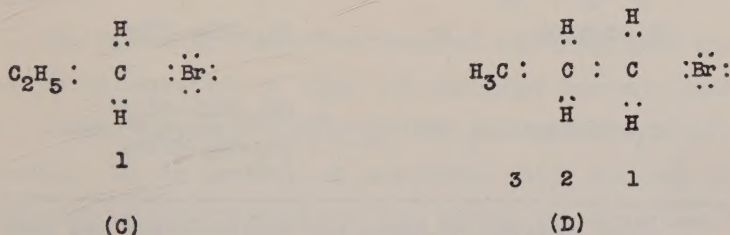
In the case of ethyl bromide, (A), two electronegative



groups, the methyl group and a bromine atom, are attached to carbon atom 1, whose electrons are therefore less firmly held than those of carbon atom 2 and more easily attacked by an oxidizing agent such as bromine. The second bromine atom should then enter the molecule in such a way as to become attached to carbon atom 1, forming 1,1-dibromoethane as the normal product.

Similarly, in isopropyl bromide, (B), two methyl groups and a bromine atom activate carbon atom 2, while carbon atoms 1 and 3 are not appreciably activated by the groups attached to them; 2,2-dibromopropane is the predicted product.

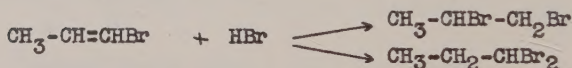
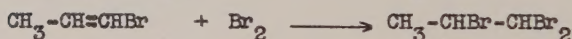
The situation is not so simple in the case of n-propyl bromide.



In considering the effects of the ethyl group and of the bromine atom on carbon atom 1, (C), it is readily seen that both tend to decrease the electronegativity of that carbon atom, making 1,1-dibromopropane the expected bromination product. However, carbon

atom 2, (D), is also activated by a methyl group,¹³ and therefore we might expect a mixture of 1,1- and 1,2-dihalides whose composition would depend upon the relative effects of the groups attached to carbon atoms 1 and 2 and upon the relative stabilities of the two products. (No 1,3-dibromopropane is expected.)

Experimentally it was impossible to obtain any pure 1,1-dibromopropane from the products of the bromination of n-propyl bromide; 1,2-dibromopropane was identified. As a matter of fact, 1,1-dibromopropane has never been prepared in pure form by any method.¹⁴ The analagous 1,1-dichloro compound, prepared from propionaldehyde and phosphorus pentachloride, is not very stable and loses hydrogen chloride readily to form alpha chloropropylene. It is to be expected that the 1,1-dibromo compound would be even less stable and would behave in a similar manner. The following equations represent reactions which might occur.



¹³The bromomethyl group has approximately the same order of electronegativity as hydrogen. This fact was not determined by hydrolysis of mercury compounds, but was estimated from addition reactions of allyl bromide and allyl chloride. Cf. Gladstone, Master's Dissertation, University of Chicago, 1935.

¹⁴Reboul prepared a mixture of 1,1- and 1,2-dibromopropane by the addition of hydrogen bromide to alpha bromopropylene. He was unable to separate the two substances. The boiling point which he reports is merely a rough estimate. Compt. rend., 79, 317 (1874).

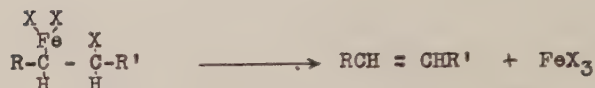
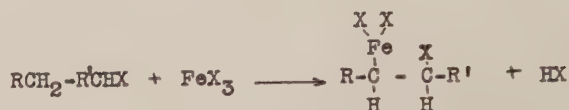
Thus, the 1,1-dibromopropane could lose hydrogen bromide to form alpha bromopropylene, which might absorb bromine to form a tribromide, or hydrogen bromide to form 1,2-dibromopropane and a small amount of 1,1-dibromopropane. The 1,1-dibromopropane would therefore possibly be almost completely removed under the experimental conditions employed.

The bromination of n-propyl bromide is a simple case in which the old empirical rules¹⁵ are not sufficient to explain or predict the experimental facts; those facts can be explained and predicted, at least in part, by a consideration of the effects of the various groups in the molecules on the different carbon atoms and by a consideration of the behavior of the final products under the conditions used. On this basis, the predicted products of the normal bromination of secondary butyl bromide would be obtained as a mixture of 2,2- and 2,3-dibromobutane. The bromination of isobutyl bromide should yield a mixture of 1,2- and 1,1-dibromo-isobutane; the latter compound would probably be decomposed, as in the case of 1,1-dibromopropane, thus leading to the isolation of only the 1,2-dibromo compound. These reactions have not been investigated.

The preceding discussion has been concerned with the process of halogenation of alkyl halides under "normal" conditions. Under "abnormal" conditions the conclusions are not applicable. In the presence of catalysts, which not only increase the velocity of substitution but also change the direction, the

¹⁵Mereshkowsky, loc. cit., offers four additional rules for substitution, based on a study of polyhalogenated compounds. They are empirical and offer no means of explaining the facts. Furthermore, it is by no means certain that normal conditions were established in the few cases where he did not use catalysts. His important generalization is that catalysts affect the direction of substitution.

reaction products are as shown by equations Ib, IIb, and IIIb. Mouneyrat's interpretation for these reactions is indicated by the following equations:¹⁶



This process may continue until polyhalogenated compounds are obtained.

Although the formation of the intermediate ferri-organic compound is not established, this mechanism is acceptable because it explains the type of product obtained. It explains not only the formation of the dihalides with the halogen atoms attached to adjacent carbon atoms, but also the large amounts of tri-, tetra-, and polyhalogeno compounds which are always found.

A question of some theoretical interest concerns the activating or deactivating effect of a halogen atom in an alkyl halide. It is well known that benzene is brominated more easily than brombenzene. The bromine atom in brombenzene is said to "deactivate" the molecule. In the aliphatic series the indications are that alkyl halides are more readily halogenated than the corresponding hydrocarbons, e.g., chlorination of pentane

¹⁶Bull. soc. chim., (3) 19, 497 (1898); 21, 618, 812 (1899); Compt. rend., 127, 274 (1898); 129, 226 (1899); Ann. de chim., (7) 20, 561 (1900).

must be stopped when only 20% of the theoretical amount of monochloride has been formed because further chlorination yields polyhalogenated compounds.¹⁷ Unfortunately, no definite conclusions can be drawn because experimental work has not been done with sufficient precautions to ensure the absence of small amounts of catalysts. Since traces of metal salts affect halogenation reactions remarkably, the available data is of little value so far as the normal reactions are concerned.

The presence of traces of iron probably accounts for the fact that in the few experiments on the chlorination of isopropyl chloride which were performed, mixtures of 1,2- and 2,2-dichloropropane were obtained.¹⁸

Experimental Part

Preparation of reagents.--Isopropyl bromide was prepared by the following method;¹⁹

Hydrobromic acid was prepared by passing sulfur dioxide through 600 grams of bromine in 700 grams of ice-water. This was placed in a 2 liter flask fitted with a mechanical stirring device and a long tube leading to a condenser. Three hundred grams of isopropyl alcohol were added and the flask warmed on a steam bath. The crude isopropyl bromide distilled as it was formed. Six hundred grams (98%) were obtained. The product was washed with cold concentrated sulfuric acid, water, aqueous sodium carbonate, and water, dried and distilled through an eight ball Snyder fractionating column. The fraction of boiling point

¹⁷B. T. Brooks, "The Non-Benzenoid Hydrocarbons," Chemical Catalog Co., New York, 1922, p. 64.

¹⁸Cf. experimental part for details.

¹⁹Organic Syntheses, 13, 21 (1933).

59.6-60.2°C. and refractive index, n_D^{20} , 1.4251 was used; the other fractions were washed again and redistilled. One hundred and sixty-five grams of pure isopropyl bromide were obtained by the two distillations. The remaining fractions boiled from 58 to 59.6°C. and had slightly low refractive indices.

Normal propyl bromide was prepared in a similar manner. Two preparations yielded products of B.P. = 70.0-71.0°, and n_D^{20} = 1.4338, 1.4340. Both preparations were practically 100% pure, since the correct refractive index is 1.4341.

Isopropyl chloride was prepared by refluxing 300 grams of isopropyl alcohol with 790 cc. of concentrated hydrochloric acid in the presence of 1390 grams of anhydrous zinc chloride for nine hours.²⁰ The isopropyl alcohol layer was separated, refluxed with an equal volume of concentrated sulfuric acid for one-half hour and then separated from the acid by distillation. Two hundred and ninety-eight grams (76%) of isopropyl chloride were obtained. This was washed in the same manner as the isopropyl bromide, dried and distilled through the Snyder column. Two hundred and thirty-nine grams, B.P. = 36.0-36.5°C., n_D^{15} = 1.3808, n_D^{20} = 1.3779, were obtained.

Bromination of isopropyl bromide.---(See Table I.)

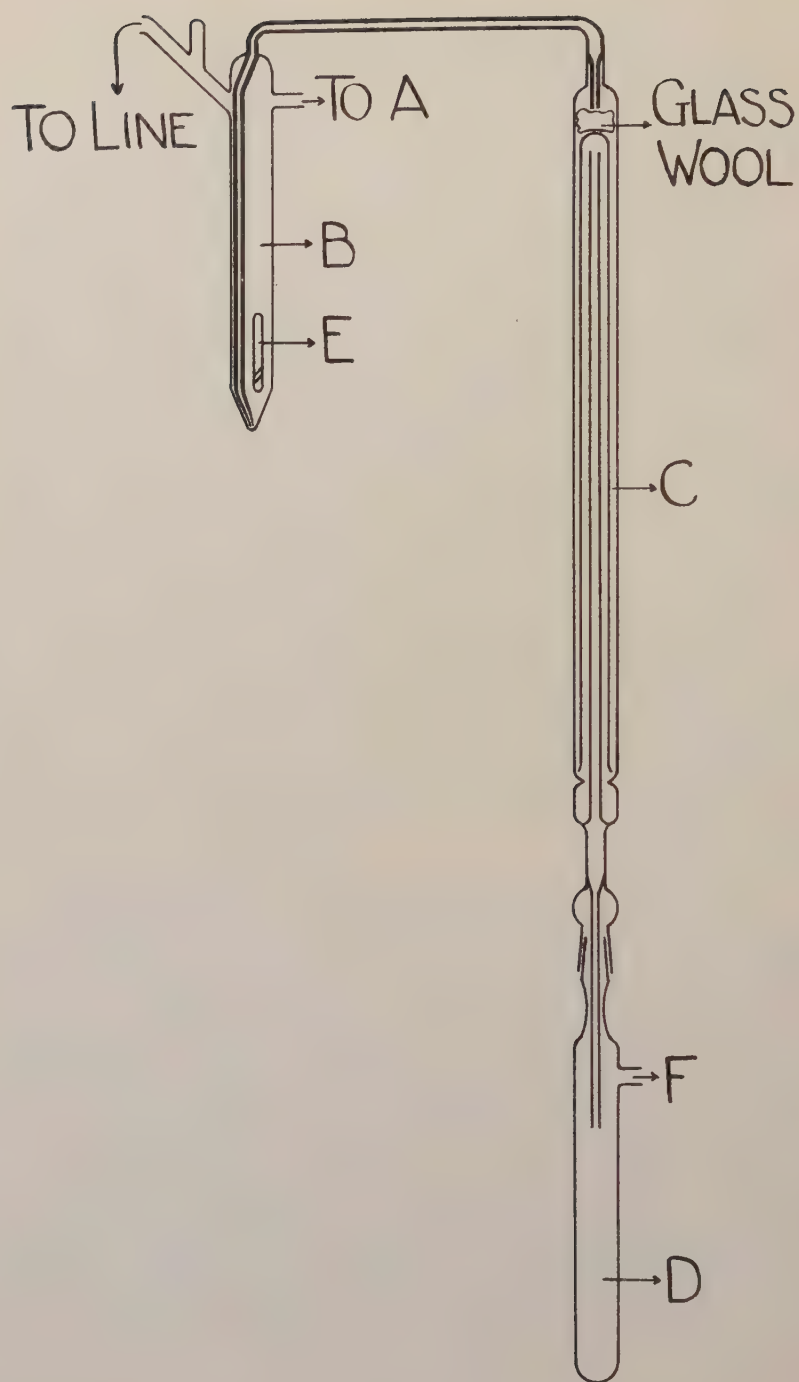
Experiment 3 is discussed in detail as an example of the application of the vacuum technique. This technique was employed to eliminate the presence of oxygen and has the advantage that the reaction time is decreased to a practical value. The need for decreasing the reaction time will become apparent when experiments 10, 11, 12, and 13 are considered.

Approximately 0.2 mol of bromine and 0.18 mol of isopropyl

²⁰Organic Syntheses, 5, 27 (1925).

bromide were introduced into containers A and B, respectively. (See diagram.) Both were frozen in liquid nitrogen baths, evacuated to a pressure of 10^{-5} mm. of mercury and allowed to warm. After the liquids had boiled, removing any dissolved oxygen, the tubes were again chilled, the system evacuated and sealed off from the line. The bromine in container A was warmed and forced into B; the mixture of bromine and isopropyl bromide after melting was stirred by means of a magnetic stirring device, E, to insure thorough mixing. The receiver, D, was chilled, first by a carbon dioxide-acetone bath and later by liquid nitrogen, thus drawing the liquid reaction mixture from B into the reaction chamber, C, which was maintained at a constant temperature by an electric furnace. As the drop of liquid entered the tube C, the drop was dispersed by a glass wool plug and the liquid vaporized just below the plug. The reaction chamber was about eighteen inches long and was so constructed that the gases passed the length of the tube three times before dropping into the receiver. The receiver was maintained at such a temperature that the pressure of the system, as recorded on a manometer attached at F, was about one-half atmosphere.

In this particular experiment the temperature of the furnace was $328^{\circ}\text{C.} \pm 5^{\circ}$ and the time required to pass all the material through the reaction chamber was three and one-half hours. The product obtained was pale yellow and became colorless as it approached room temperature, which indicated the presence of olefines and a small amount of bromine. The product was distilled in vacuo to remove any high boiling material, the distillate being collected at -80° . The distillate was washed with cold concentrated sulfuric acid, once with water, once with a saturated aqueous sodium bicarbonate solution, twice with water,



and dried over sodium sulfate. (In experiments in which the material obtained from the reaction chamber was colored, the unreacted bromine was removed by washing with a concentrated solution of sodium carbonate before washing with sulfuric acid.) The dried product was distilled from a small flask to which was sealed a small indented fractionating column. In order that the boiling points of the various fractions might be properly interpreted, the temperature was recorded for every 0.5 cc. of distillate and in special cases for every 0.1 cc.

cc.	B.P., °C.	cc.	B.P., °C.	cc.	B.P., °C.
0.0 (1st drop)	55.0	6.0	63.0	10.7	115.2
		6.1	61.0	11.2	116.0
0.5	59.5	6.2	80.0	11.6	119.0
1.0	60.2	6.3	106.0		
1.5	61.0	6.4	110.0		
2.0	61.0	6.8	112.0		
2.5	60.8	7.2	113.2		
3.0	61.5	7.7	114.0		
3.5	62.0	8.2	114.0		
4.0	63.0	8.7	114.2		
4.5	62.5	9.2	114.8		
5.0	61.5	9.7	114.0		
5.5	63.0	10.2	114.5		

The substances which could have been present in the mixture which was distilled are isopropyl bromide, 1,2-dibromopropane, 2,2-dibromopropane and higher bromination products. The physical constants of these materials are as follows:²¹

	B.P., °C.	n_D^{20}
Isopropyl bromide	59.6	1.4341
1,2-dibromopropane	140	1.5203, 1.5194
2,2-dibromopropane	114	1.4977
Tribromopropanes	>190	~1.55

²¹The boiling point and refractive index of 2,2-dibromopropane were determined from a sample obtained by redistilling the product of experiment 2, Table I. The values which were determined agree exactly with those determined by Kharasch, J. G. McNab, and M. C. McNab, J. Am. Chem. Soc., 57, 1463 (1935), on a sample obtained by the addition of hydrogen bromide to methyl acetylene.

The constants for the other substances are taken from the International Critical Tables.

An examination of the boiling point record shows that isopropyl bromide, 2,2-dibromopropane and a trace of higher boiling material were obtained. No 1,2-dibromopropane was present; if it had been one of the reaction products it would not be removed by the vacuum distillation and consequently should be observed in the final distillation. The refractive indices of the different fractions were taken to confirm the conclusions drawn from the boiling points, and the compositions of the fractions were estimated from the refractive indices. The results of "run" number 3 are summarized in the following table:

Fraction	B.P. °C.	gms.	n_D^{20}	Conclusion
(1)	59.5- 63	8.0	1.4272	~ 97% isopropyl bromide
(2)	80 -112	1.3	1.4664	~ 54% isopropyl bromide ~ 36% 2,2-dibromopropane
(3)	113 -116	8.1	1.4980	99+% 2,2-dibromopropane
(4)	116 -119	0.6	1.5003	

It should be noted that the refractive index is used only as a confirmatory test. For example, in fraction (3), the refractive index alone would mean nothing because it could be the refractive index of a mixture of isopropyl bromide and any of the bromides of n_D greater than 1.4980. However, the boiling point shows that only 2,2-dibromopropane could be present. Similarly, the composition of a mixture, such as fraction (2), is determined qualitatively from the boiling range and semi-quantitatively from the refractive index. It must be clear that neither the boiling point nor the refractive index, alone, is sufficient to determine the composition of a product, but that together they are satisfactory.

Experiments 1 to 4 were carried out in the same way; in all four cases the only dibromide obtained was 2,2-dibromopropane. Carefully washed asbestos fiber was then introduced between the

outer and first inner tubes of the reaction chamber to act as a surface upon which ferric chloride could be deposited. The asbestos was tested for the presence of catalysts by brominating isopropyl bromide in the manner previously described. In this experiment the bromine was distilled in the line and no ferric chloride was added. The products were 2,2-dibromopropane and tribromides. (Number 5.)

In experiment 6 an open side tube was sealed to the capillary tube just above the point at which it entered the reaction chamber. That tube served as an inlet for a mixture of 3% oxygen in nitrogen, which passed through the system from a gasometer while the isopropyl bromide-bromine mixture was drawn from B into D. A bubble counter at F replaced the manometer. A higher concentration of oxygen could not be used because of the possibility of oxidizing the isopropyl bromide. The only dibromide obtained was 2,2-dibromopropane. Oxygen has no effect on the direction of substitution.

Numbers 7 and 9 were performed in the same manner as number 5 with the following modifications: anhydrous ferric chloride (0.0019 and 0.0006 mols, respectively) was dissolved in the isopropyl bromide; lower temperatures were used. The only dibromide found among the reaction products was 1,2-dibromopropane. Ferric chloride definitely changes the direction of substitution.

In experiment 8, in which 0.0006 mol of ferric chloride was dissolved in isopropyl bromide and the procedure of number 6 employed, 1,2-dibromopropane was obtained.

Numbers 10 and 11 are bomb tube experiments. The bromine and isopropyl bromide were placed in separate tubes which were connected to a central bomb tube. After the contents of the tubes

had been frozen, the system was evacuated, warmed, evacuated again and sealed off from the line. The reactants were distilled into the central bomb tube and the tube was sealed. The bomb tube was heated for a given period of time and then opened; the contents were washed in the usual manner and distilled. Both experiments yielded large quantities of tribromopropanes. Number 10 (heated at 150° for four hours) yielded a mixture which definitely contains tribromides and unreacted isopropyl bromide. The presence of dibromides can not be shown. The boiling points at 0.5 cc. intervals are as follows:

cc.	B.P.	cc.	B.P.	cc.	B.P.
0	55.0	3.0	59.5	6.0	188
0.5	59.5	3.5	106.5	6.5	189.5
1.0	61.0	4.0	115.0	7.0	191
1.5	62.0	4.5	165	7.5	193
2.0	61.0	5.0	171	8.0	194
2.5	60.0	5.5	168		

In number 11 (heated at 100° for 89 hours), the presence of isopropyl bromide, tribromides and a small amount of 1,2-dibromopropane was demonstrated.

The formation of the relatively large quantities of tribromides can be explained in two ways. First, the bomb tubes may have contained a trace of mineral salts, even though the tubes had been rinsed ten times with distilled water after they had been cleaned. This would explain the formation of both the 1,2-dibromopropane and the tribromides. Second, it may be that the dihalide is more readily brominated than the monohalide because of an activating influence of the bromine atoms, thus leading to the formation of polybromides. The long period of heating the reaction mixture without adequate stirring is an optimum condition for the influence of either of these factors. It is impossible to decide which factor is the more important; probably both are

effective.

Since it was demonstrated that oxygen had no effect on the direction of substitution, the last two experiments recorded in Table I were carried out by simply refluxing a large excess of isopropyl bromide with bromine in an all-glass apparatus for several days. This method has the advantage of keeping the reactants well agitated. The products were identified by the previously described methods.

In number 12, 2,2-dibromopropane and tribromides were found. No 1,2-dibromopropane was present. In number 13, 2,2-dibromopropane and a trace of either 1,2-dibromopropane or a tribromide were obtained. To again demonstrate the sharp separation of the various fractions, the boiling point record of number 12 (after the large excess of unreacted material had been removed in the first fraction) is shown.

cc.	B.P.°C.	cc.	B.P.°C.
55	63.0	69.5	117
58	67.0	70.0	117
60	70.0	70.5	116.5
65	71.5	71.0	115
65.5	84	71.5	112
66.0	95	72.0	116
66.5	103	72.5	120
67.0	110	73.0	121
67.5	113	73.5	123
68.0	114	75.0	129
68.5	115	75.5	180
69.0	117	76.0	187

When the reflux method of bromination is used, it is necessary that the apparatus be scrupulously clean. In one case the apparatus was rinsed with distilled water which contained some minute solid particles; only 1,2-dibromopropane was then obtained. (B.P.= 139-140.5°; n_D^{20} = 1.5199.) In numbers 12 and 13, in which the apparatus was washed with redistilled water, the product was 2,2-dibromopropane.

Bromination of n-propyl bromide.--(See Table II.)

Bromination of n-propyl bromide by the vacuum technique (numbers 1 to 4, Table II), yielded tribromides as the main product. Only in number 2 was there any definite evidence of a dibromide.

When the reaction was carried out in a bomb tube or by refluxing the reagents, the main product was 1,2-dibromopropane. A possible explanation of these facts is given on page 6.

Chlorination of isopropyl chloride.--(See Table III.)

Chlorine, after passing through two wash bottles containing concentrated sulfuric acid and one filled with glass wool, was bubbled through isopropyl chloride under the conditions recorded in Table III. In experiments 4 and 5 the apparatus was illuminated by means of a 500 watt bulb. In number 5, dry oxygen and chlorine were bubbled through the isopropyl chloride simultaneously. The method of analysis was the same as that used in the bromination experiments.

In all cases, mixtures of 1,2- and 2,2-dichloropropane were obtained, together with some trichloro compounds.²² The formation of the relatively large quantities of 1,2-dichloropropane may possibly be explained by the fact that the chlorine was not sufficiently pure and may have contained traces of catalysts. This was not investigated further.

Thermal stability of n-propyl and isopropyl bromides.--

At high temperatures n-propyl bromide is converted into isopropyl bromide. Aronstein found that 26 grams of the former, when heated

²²The physical constants of the materials involved are as follows:

	B.P., °C.	n_D^{20}	n_D^{15}
Isopropyl chloride	36.5	1.3779	1.3808
1,2-dichloro- propane	96.8	1.4389 (?)	
2,2-dichloro- propane	69.7	1.4093	
Trichloropropanes	123, 137, 158		

TABLE I
BROMINATION OF ISOPROPYL BROMIDE

No.	Mols of Isopro- pyl Bro- mide ^a	Conditions and Technique	Temp. ±5°C.	Time in Hrs.	Recovery in Gms. b	Fractions			Con- clusions ^c
						B.pt., °C.	Gms.	n _D ²⁰	
1	0.21	Vacuum	300	..	6.3	112-113	2.4	1.4880	88% 2,2
2	0.21	Vacuum	305	3½	14.8	112-114	4.4	1.4945	96% 2,2
3	0.21	Vacuum	328	3½	19.0	80-112	1.3	1.4660	
						113-116	8.1	1.4980	100% 2,2
						116-119	0.6	1.5003	
4	0.21	Vacuum	350	2	19.8	110-112	1.7	1.4862	
						113-116	11.1	1.4988	95% 2,2
						117-121	2.4	1.5020	
5 ^d	0.22	Vacuum with asbestos	350	2	12.4	109-111	0.4		
						113-116	3.0	1.5008	90% 2,2
						117-156	4.0	1.5081	
6	0.22	3% O ₂ in N ₂ ; at 1 atm.	338	2	26.5	85-113	1.9	1.4957	>90% 2,2
						113-116	7.0	1.5000	>90% 2,2
7	0.22	Vacuum with 0.3 gms. FeCl ₃	154	1½	15.3	65-138	1.5	1.4469	
						138-140	5.0	1.5196	100% 1,2
8	0.23	3% O ₂ with 0.1 gm. FeCl ₃ at 1 atm.	176	¾	12.4	65-138	1.4	1.4806	
						139-140.5	5.0	1.5199	100% 1,2
9	0.22	Vacuum with 0.1 gm. FeCl ₃	175	1	14.6	65-138	0.4		
						138-140	1.8	1.5086	88% 1,2

TABLE I--CONTINUED

No.	Mols of Isopropyl Bromide ^a	Conditions and Technique	Temp. $\pm 0.5^\circ\text{C}$.	Time in Hrs.	Recovery in Gms. b	Fractions			Conclusions ^c
						B.pt., $^\circ\text{C}$.	Gms.	n _D ²⁰	
10	0.11	Bomb tube evacuated to 10-5 mm. Hg.	150	4	15.4	106.5-115	0.7	1.4800	
						165-171	3.0	1.5430	
						188-194	6.0	1.5700	
11	0.11	Same as 10	100	89	11.5	60-138	0.6	1.4718	
						142-145	2.0	1.5225	95% 1,2
						183-190	3.2	1.5610	
12	0.98	Reflux	Steam bath	143	112.8	84-110	3.1	1.4522	
						113-117	9.4	1.4970	99% 2,2
						117-129	6.1	1.5040	>90% 2,2
						180-187	3.3		
13	0.89	Reflux	Steam bath	143	82.2	59-112	67.0		
						113-116	7.0	1.4978	100% 2,2
						117-145	2.1		

^aIn Nos. 10 and 11, 0.10 mol of bromine; in 12 and 13, 0.17 mol of bromine; and in all other cases, 0.18 mol of bromine were used.

^bThe "recovery" reported is the total weight before the final distillation. The difference between these values and the sum of those in the eighth column is accounted for by recovered unreacted material and residue.

^cThe figures in this column, based upon the fact that the refractive index is a linear function of the composition, refer to the fractions indicated.

^dIn nos. 5-9, inclusive, washed and ignited asbestos was introduced between the outer and intermediate walls of the tube C.

TABLE II
BROMINATION OF n-PROPYL BROMIDE

No.	Mols of n-propyl Bromide ^a	Conditions and Technique	Temp. ±50C.	Time in Hours	Recovery in Gms. ^b	Fractions			Con- clu- sions ^c
						B.Pt., °C.	Gms.	n ²⁰ D	
1	0.21	Vacuum	350	2½	16.5	72-165 165-180	6.0 1.4	1.5210 1.5673	
2	0.21	Vacuum	310	2¾	21.6	74-139 138-147 178-184	3.5 8.0 2.1	1.4463 1.5372 1.5850	70% 1,2
3	0.22	Vacuum	311	1½	28.7	73-130 134-140 141-148 170-233	6.6 1.0 1.5 8.4	1.4378 1.5129 1.5214 1.5905	85% 1,2 98% 1,2
4	0.39	Vacuum	305	1	12.3	79-125 125-136 68-75/5mm.	2.6 0.6 3.0	1.4420 1.5025 1.5662	
5	0.11	Bomb tube	150	4½	15.5	133-138 139-144 180-185	2.0 8.1 3.2	1.5103 1.5211 1.5600	90% 1,2 96% 1,2
6	1.02	Reflux	Steam bath	114	113	72-131 131-139 139-141 141-146	3.3 6.3 14.9 3.8	1.4440 1.5151 1.5190 1.5203	> 99% 1,2

^aIn No. 5, 0.10 mol of bromine was used, and in all other cases 0.18 mol of bromine.

^{b,c}See Table I.

TABLE III
CHLORINATION OF ISOPROPYL CHLORIDE

No.	Mols of Isopropyl Chloride	Condi- tions	Time in Hrs.	Re- covery in Gms.	Fractions			Con- clusions
					B.P. °C.	Gms.	n_D^{20}	
1	0.38	27°	2	18.2	34.5-45	11.7	1.3781	
					65-98	5.5	1.4235	52% 1,2 48% 2,2
2	0.38	Reflux	4	19.6	34-40.8	9.0	1.3796	
					40.8-68	0.8	1.4083	
					68-70.5	3.4	1.4150	87% 2,2 13% 1,2
					70.5-105	5.4	1.4362	
3	0.59	Reflux	9½	29.6	39-67	2.8	1.4050	
					68-71	3.2	1.4139	84% 2,2
					72-95	13.3	1.4250	53% 1,2 47% 2,2
					96-98	0.9	1.4379	96% 1,2
					99-120	4.7	1.4470	
4	0.79	0-5°; light	3	47.1	34-68	39.5	1.3820	
					69-71	0.6	1.4128	89% 2,2
					72-95.5	5.0	1.4295	68% 1,2 32% 2,2
5	0.79	0-5°; light; oxygen	3	38.3	36-68	31	1.3825	
					69-71	1.5	1.4131	88% 2,2
					72-95	2.5	1.4250	53% 1,2 47% 2,2
					95-95.5	1.5	1.4389	100% 1,2

at 280° for 27 hours, formed 11 grams of the latter.²³ In this work, high temperatures were reached only in the vacuum experiments, and there for relatively short periods of time; it was shown that very little isomerization occurred.

Isopropyl bromide was passed through the reaction tube at 350°. It was slightly decomposed and was therefore washed and dried as usual. In spite of mechanical losses, 77% of the pure isopropyl bromide ($n_D^{20} = 1.4250$) was recovered.

Normal propyl bromide was subjected to similar treatment; 81% ($n_D^{20} = 1.4340$) was recovered.

It was also shown that 2,2-dibromopropane can be heated for several hours at 150° with only slight decomposition.

²³Aronstein, Ber., 14, 608 (1881).

SUMMARY

1. Bromination of isopropyl bromide yields 2,2-dibromopropane if no metals or salts are present.
2. In the presence of ferric chloride, bromination of n-propyl or isopropyl bromide yields 1,2-dibromopropane.
3. In the bromination of n-propyl bromide under normal conditions, no 1,1-dibromopropane was identified.
4. Oxygen has no apparent effect on the direction of substitution.
5. Chlorination of isopropyl chloride yielded mixtures of 1,2- and 2,2-dichloropropane.
6. These facts have been discussed and an explanation has been offered.

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